Nondestructive Olive Quality Detection Using FT-NIR Spectroscopy in Reflectance Mode

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Abstract

Quality features including firmness, oil content, and color (chroma, hue) of two olive (*Olea europaea* L.) varieties ('Ayvalik' and 'Gemlik') were predicted using FT-NIR spectroscopy. Reflectance measurements of intact olives were performed using a bifurcated fiber optic probe. Measurements of firmness, oil content, and color values were done following the spectral measurements using standard methods. Calibration methods were developed using the partial least squares method. Good correlations were obtained in calibration and validation for Magness-Taylor (MT) maximum force, which was used as a measure of firmness, for both 'Ayvalik' and 'Gemlik' varieties; the coefficient of determination (R^2) for 'Gemlik' olives was 0.74 (SEC = 1.27) in calibration and 0.67 (SEP = 1.37) in validation. Better oil content prediction of olive fruits was obtained for the pooled data of 'Ayvalik' and 'Gemlik' varieties with the R^2 value of 0.64 (SEP = 0.05) in validation. Higher correlations were obtained for color predictions with R^2 = 0.88 and SEP = 12.9 for chroma and R^2 = 0.86 and SEP = 0.10 for hue for 'Gemlik'. Similar color prediction results were obtained for the 'Ayvalik' variety.

INTRODUCTION

Olives, which are produced by different growers, often are at different maturation stages with different oil content, firmness and color values, and are mingled in the bins when they are brought to the olive processing plants. Applying the same processing procedures on olives with different properties tends to produce insufficient quality in final products such as olive oil or table olives. Sorting olives in terms of inner and surface properties prior to processing would result in high quality final products, thus providing enormous benefits for both consumers and producers.

Unripe olives would cause problems in the fermentation process, as these olives have poor skin permeability and a low flesh-to-stone ratio (Kailis and Harris, 2004). Similarly, overripe olives tend to get soft quickly. Moreover, olives are susceptible to damage when mechanical grading systems are used. Traditional quality sensing equipment does not have the capability of sensing inner and outer olive quality. Hence, there is a need for new sorting/grading systems using optical detection techniques that would cause minimal or no damage to olives.

Near infrared (NIR) technology has the advantage of sensing inner and superficial characteristics of agricultural products nondestructively. Significant progress has been made recently in application of NIR technology for inspecting agricultural products. Most reported research has used the diffraction-type instruments. Lammertyn et al. (1998) used NIR spectroscopy for detection of acidity, soluble solids content and firmness of Jonagold apples. McGlone and Kawano (1998) determined dry-matter and soluble solids contents of kiwifruit using NIR spectroscopy. More recently, the Fourier transform NIR (FT-NIR) technique, as a good alternative to diffractive NIR spectroscopy, has been applied for noninvasive fruit quality detection (Peirs et al., 2002; Ying et al., 2005).

This study was aimed at detecting quality of intact olives including firmness, oil content, and color, using FT-NIR spectroscopy. Statistical models were developed using the partial least squares (PLS) method for relating spectral measurements to the quality attributes of olives.

MATERIALS AND METHODS

Olives

Two varieties of olives (*Olea europaea* L. cv. 'Ayvalik' and 'Gemlik') were used in the study. An olive tree for each variety was selected from the olive orchard of the Directory of Edremit Olive Growing Station for this study. Olives were harvested once a week for a period of six weeks starting on October 12 and ending on November 16, 2006. A total of 463 olives, 254 for 'Ayvalik' and 209 for 'Gemlik', were chosen from the harvested olives based on their size, maturation stage and the absence of surface defects. The olive samples were kept at cold storage (7°C) during the nights between the days of measurements. Spectroscopic measurements were taken from the olives after they had been brought into equilibrium with the room temperature of 25°C.

Spectroscopic Measurements

On the day following harvest, spectral measurements were first taken on olives in reflectance mode using a FT-NIR spectrometer, followed with measurements of size and color of olives. On the following two days, firmness was measured and oil was extracted from each olive.

Spectral measurements were performed in reflectance mode using a Bruker MPA (Multi-Purpose Analyzer) FT-NIR spectrometer (Bruker Optik, GmbH, Ettlingen Germany) equipped with an InGaAs detector and a high intensity NIR light source (tungsten-halogen). The wavelength region scanned with the fiber optic probe (type IN 261) was from 780 nm to 2500 nm. Thirty-two scans were performed per spectrum. Resolution was 8 cm^{-1}. Instrument control and spectra analysis were performed using OPUS software. In all the applications, the Blackman-Harris-3-term apodization function, a phase resolution of 64 cm^{-1}, a power spectrum phase correction method, and a zero filling factor value of 2, were used.

Reflectance spectra were obtained from both a reference (Spectralon®) and sample consecutively for each sample. The fiber optic probe was placed directly on the equatorial surface of the fruit during spectral measurements. The fiber optic probe used had a bifurcated optical configuration, which guided the light to the sample by the source fibers and received the reflected light with the detector fibers (Fig. 1). In the measuring head of the fiber optic probe, the source and detector fibers were mingled randomly, forming a sensing area of about 11.7 mm^2.

Physical Measurements

Measurements of the physical properties of olives were done following the spectral measurements. These measurements were color, weight, size (diameter and length), firmness, and oil content (Table 1).

Olive tissue firmness was measured without removing skin with a Chatillon penetrometer, model DFS-500 (John Chatillon Sons, Inc. New York, NY, USA) using a flat-head stainless-steel cylindrical probe with a 2 mm diameter. Penetration depth of the probe into the flesh of the olive fruit was approximately 3 mm (the flesh thickness of the samples ranged between 3.5 to 5.5 mm for both olive varieties). Strain energy (i.e., the area under the force/deformation curve until the maximum force, N-mm), slope (N/mm, ratio of force to the deformation until the maximum force), and maximum force (N) were extracted from the force/deformation curves and were considered to be the measures of fruit firmness.

Color was measured using a colorimeter (Model CR-200, Minolta, Japan). Color readings were recorded in the format of CIE XYZ color space (also known as CIE 1931 color space). It was then converted into Lab color space (CIE $L^*a^*b^*$), which is an absolute color space. Chroma ($\sqrt{a^{*2}+b^{*2}}$) and hue (arc tan [b^*/a^*]) were derived from Lab color space.

Extraction of oil was performed on each olive fruit separately. In preparation of the sample for oil extraction, the kernel of each fruit was removed from the fruit flesh and only the oil in the flesh of each olive fruit was extracted. Olives were weighed individually. Extraction of oil from the flesh of the fruit was performed using a Soxhlet extraction method by crushing the olive flesh in a mortar, then applying solvents and filtering.

Spectra Analysis

Relative spectra of the samples were obtained directly from the software as a result of the following calculation:

$$\text{Relative spectra} = \frac{sample}{reference}$$

The wavelength range between 780 nm and 2500 nm for the fiber optic probe was divided into five sub groups; they were analyzed to find the optimal sub wavelength ranges that would yield the best correlations between the physical parameters and the spectroscopic measurements. Calibration and validation models were developed using the partial least squares method (PLS) based on leave-one-out cross validation technique for predicting firmness, oil content, skin chroma and hue. In the leave-one-out cross validation method, calibration is performed by leaving one sample out, and using that single sample in validation. This process is repeated until all the samples have been used in validation once. The performance of the calibration model is determined based on the averages of the repeated procedures separately in calibration and validation.

Different processing techniques were applied on olive spectra, before PLS analysis, to find out if processing the spectra would improve the performances of the calibration models. For this purpose, spectra of olives were used in three different ways in the procedures of developing calibration models. First, the relative spectra after acquisition were used without any pre-processing except smoothing. Second, the following spectrum processing techniques were applied on the olive spectra, one at a time and before the PLS analysis: constant offset elimination, min-max normalization, vector normalization, straight-line subtraction, first derivative, second derivative, multiplicative scattering correction. Finally, two processing techniques, one after another, were applied on olive spectra after spectroscopic measurements: first derivative and straight-line subtraction, first derivative and vector normalization, and first derivative and multiplicative scattering correction. Mean centering was applied on all the processed spectra. Data for the two olive varieties were evaluated separately for each variety and also together as one data group (pooled). The OPUS software was used in establishing the calibration models and for performing the validations. The coefficient of determination, the standard error of calibration (SEC), and the standard error of prediction (SEP) were used to evaluate the performance of the calibration models.

This paper reports on results obtained from PLS applications between the spectroscopic and physical measurements using three different data groups ('Ayvalik', 'Gemlik' and the pooled data of the two varieties) and different data treatment applications. Primarily, the optimal results obtained from different applications are reported here.

RESULTS AND DISCUSSION

Measurements of Olive Quality

Firmness values of the two varieties were close to each other as can be seen in Table 1 although the firmness value for 'Ayvalik' variety was slightly higher than that of

'Gemlik'. The change of firmness vs. harvest time for the two olive varieties was quite similar; it decreased steadily from the initial week towards the last week. Firmness prediction was performed for each firmness parameter (i.e., max force, slope, and area) separately. Best results were obtained when using MT maximum force and partly using MT slope.

Color values of the two olive varieties were close to each other although they were slightly higher for the 'Ayvalik' variety (Table 1). On the other hand, the two olive varieties had different amounts of oil; the average oil content for a single 'Ayvalik' olive fruit was almost double that of a single 'Gemlik' olive fruit. The oil content increased with the harvest date. The increase of oil content with time was more pronounced for the 'Ayvalik' variety compared to 'Gemlik'.

Reflectance Spectra of Olives

There were clear differences between the average absorbance spectra of olives harvested in the beginning, in the middle, and at the end of the harvest period (Fig. 2). Peaks at 970, 1210, 1440, 1720, 1760, 1930, and 2300 nm existed in the spectra. At 970, 1440, and 1930 nm, absorbance was the highest for the olives harvested the earliest and the lowest for the olives harvested the latest. On the other hand, absorbance was the highest for the olives harvested the latest and the lowest for the olives harvested the earliest at 1210, 1720, 1760 (weakly at 1830), and 2300 nm respectively. Wavelengths of 970, 1210, and 1440 nm are close to the water absorption wavebands.

Firmness Prediction

As can be seen from Table 2 and Fig. 3a, firmness was predicted most effectively using MT maximum force for both 'Ayvalik' (R^2 = 0.65, SEP = 1.82) and 'Gemlik' (R^2 = 0.67, SEP = 1.37) varieties and also for the pooled data of the two varieties (R^2 = 0.66, SEP = 1.71). Relatively poor predictions were obtained for MT slope or MT area (Table 2). While all the peaks in the spectrum of olives (Fig. 2) were in the effective wavelength range determined for the 'Ayvalik' variety, only peaks at 1720, 1760, and 2300 nm were used for firmness prediction of 'Gemlik' variety (Table 3). The wavelength at 970 nm, which was among the effective wavelengths determined for firmness prediction for 'Ayvalik' varieties, was determined as the pectin absorbance band from the NIR spectra data of apples and citrus (Elvidge, 1990). This same wavelength was also reported to be a strong peak for water and carbohydrate absorption (McGlone and Kawano, 1998). Wavelength ranges between 947-977 nm, 1120-1205 nm, and 1342-1492 nm were reported to have high loading weights for stiffness in apples (Lammertyn et al., 1998). This finding is in agreement with the effective wavelengths (970, 1210, and 1440 nm) determined for olive firmness. Peirs et al. (2002) reported that the wavelength range of 1000-2000 nm was effective in predicting firmness, soluble solids content, and acidity of apples.

Oil Content Prediction

Optimal oil content prediction results were obtained for the pooled data of the 'Ayvalik' and 'Gemlik' varieties (R^2 = 0.64, SEP = 0.05) (Fig. 3b, Table 2). The coefficient of determination obtained was 0.68 for calibration (SEC = 0.04). Values of SEP and SEC determined for oil content prediction were close to each other, indicating good performance of the model (Lammertyn et al., 1998). When the prediction models were developed for each variety, better oil content predictions were obtained for the 'Ayvalik' variety than for 'Gemlik', although the predictions were not as good as those for the pooled data (Table 2).

Extracting oil from olive fruits was a challenging task because it was quite time consuming and needed considerable effort. The extraction process could be susceptible to error, which might have negatively affected the model performance. Moreover, the olive samples tested did not have a large range of oil content. In detection of dry matter (DM) and soluble solids content (SSC) in kiwifruit by NIR spectroscopy, McGlone and Kawano

(1998) emphasized that adequate variation was needed in the data set as well as in origin, age, size, and firmness of the samples.

The effective wavelength ranges and spectrum processing methods determined for oil content prediction are given in Table 3. Wavelengths between 800-1334 nm and between 1639-1836 nm were found to be effective in oil content prediction (Table 3 and Fig. 2). Included in the effective wavelength ranges were peaks at 970, 1210, 1760, and 1836 nm. Peaks at 970 and 1210 nm are close to the water peaks in the fruit. Among the different spectra processing methods, the "min-max normalization" spectrum processing method was most effective for oil content prediction. Average spectra of 'Ayvalik' were quite similar to the ones for 'Gemlik' olives shown in Figure 2; therefore, average spectra of 'Ayvalik' and the pooled data were not given.

Color Prediction

Good validation results were obtained for both color parameters (chroma and hue) for each data group (Table 2). Better prediction of chroma was obtained for the 'Gemlik' variety (Fig. 3c; Table 2) with the coefficient of determination of $R^2 = 0.88$ (SEP = 12.9). For 'Ayvalik' variety, the optimal validation result for chroma was obtained with $R^2 = 0.83$ (SEP = 15.1). Results of the prediction models for hue were close for all three data groups (Table 2); the R^2 values were 0.85, 0.86, and 0.82 for the 'Ayvalik', 'Gemlik', and pooled data groups respectively (Table 2; Fig. 3d), with the corresponding SEP of 0.11, 0.10, and 0.12.

The effective wavelength ranges and spectrum processing methods determined for optimal prediction of chroma and hue are given in Table 3. The effective wavelength range for chroma was between 800-1836 nm while the spectrum processing methods were "first derivative" and "vector normalization" for the 'Gemlik' data group. The effective peaks in the wavelength range mentioned above were 970, 1210, 1440, 1720, and 1760 nm. For predicting hue for the 'Ayvalik' data group, the effective wavelength ranges were 800-1334 nm and 1639-1836 nm, and the spectral data processing methods were "straight-line subtraction." Peaks for the two effective wavelength ranges given above were 970 and 1210 nm for the first and 1720 and 1760 nm for the second respectively.

The findings of this research showed that FT-NIR spectroscopy has good potential for nondestructive detection of inner and superficial olive quality constituents.

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Tables

Table 1. Some physical properties of 'Ayvalik' and 'Gemlik' olives.

Variety (number of samples)		MT Firmness			Color		Oil Content (g)
		Maximum force (N)	Area (N-mm)	Slope (N/mm)	Chroma	Hue	
Ayvalik (254)	Average	4.53	7.43	1.42	38.86	0.14	0.21
	S.D.	3.03	3.00	1.66	33.72	0.25	0.08
Gemlik (209)	Average	4.07	7.41	1.10	41.79	0.24	0.12
	S.D.	2.40	3.00	1.21	35.03	0.25	0.05
Pooled (463)	Average	4.33	7.42	1.27	40.14	0.19	0.16
	S.D.	2.77	3.00	1.48	34.34	0.25	0.08

Table 2. Summary of calibration and validation results for the firmness, oil content, chroma and hue for 'Ayvalik' and 'Gemlik' varieties.

Feature	Data group	Data processing	Factors	Calibration R^2	Calibration SEC	Validation R^2	Validation SEP
Firmness MT_Max Force	Ayvalik	FD	11	0.73	1.61	0.65	1.82
	Gemlik	MSC	11	0.74	1.27	0.67	1.37
	Pooled	VN	12	0.68	1.64	0.66	1.71
Firmness MT_Area	Ayvalik	COE	9	0.42	2.33	0.39	2.42
	Gemlik	NSDP	10	0.48	2.21	0.35	2.44
	Pooled	NSDP	11	0.43	2.28	0.38	2.41
Firmness MT_Slope	Ayvalik	VN	11	0.51	1.19	0.42	1.29
	Gemlik	MSC	7	0.47	0.90	0.40	0.95
	Pooled	MMN	14	0.51	1.05	0.43	1.15
Oil Content	Ayvalik	SLS	10	0.60	0.05	0.49	0.06
	Gemlik	COE	4	0.32	0.04	0.32	0.04
	Pooled	MMN	12	0.68	0.04	0.64	0.05
Chroma	Ayvalik	SLS	11	0.87	13.5	0.83	15.1
	Gemlik	FD+VN	9	0.91	11.5	0.88	12.9
	Pooled	FD+SLS	11	0.88	12.7	0.84	14.8
Hue	Ayvalik	SLS	9	0.87	0.10	0.85	0.11
	Gemlik	FD+VN	10	0.91	0.08	0.86	0.10
	Pooled	FD+SLS	12	0.85	0.11	0.82	0.12

R^2: Coefficient of determination; SEC (SEP): Standard error of calibration (prediction); COE: Constant offset elimination, MSC: Multiplicative scattering correction, MMN: Min-max normalization, SLS: Straight line subtraction, FD: First derivative, VN: Vector normalization, NSDP: No spectral data processing.

Table 3. Effective wavelength ranges and spectrum processing methods for optimal firmness predictions for 'Ayvalik' and 'Gemlik' varieties.

Data group	Constituent	Wavelength range (nm)	Peaks (nm)	Processing
Ayvalik	Firmness	800-2355	All the peaks	FD
Gemlik	Firmness	1640-1837	1720, 1760	MSC
		2173-2355	2300	
Pooled	Oil content	800-1334	970, 1210	MMN
		1639-1836	1760, 1836	
Gemlik	Chroma	800-1836	970, 1210, 1440, 1720, 1760	FD+VN
Ayvalik	Hue	800-1334	970, 1210	SLS
		1639-1836	1720, 1760	

FD: First derivative, MSC: Multiplicative scattering correction, MMN: Min-max normalization, SLS: Straight line subtraction, VN: Vector normalization.

Figures

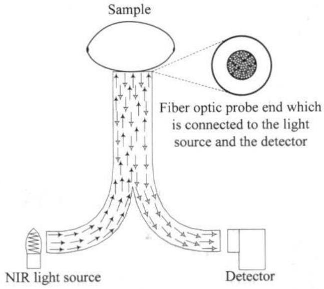

Fig. 1. Schematic view of the reflectance measurement performed using fiber optic probe.

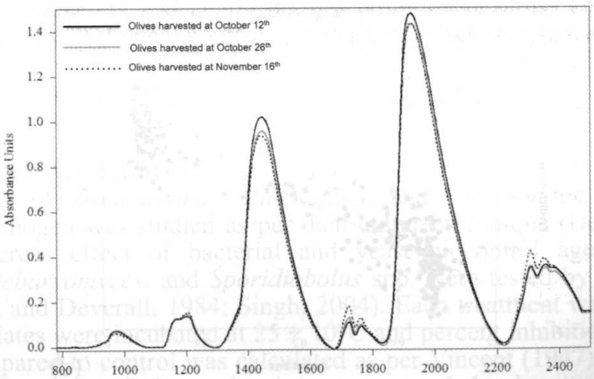

Fig. 2. Average relative absorbance spectra of 'Gemlik' olives obtained in reflectance mode at the beginning, in the middle and at the end of the harvest period.

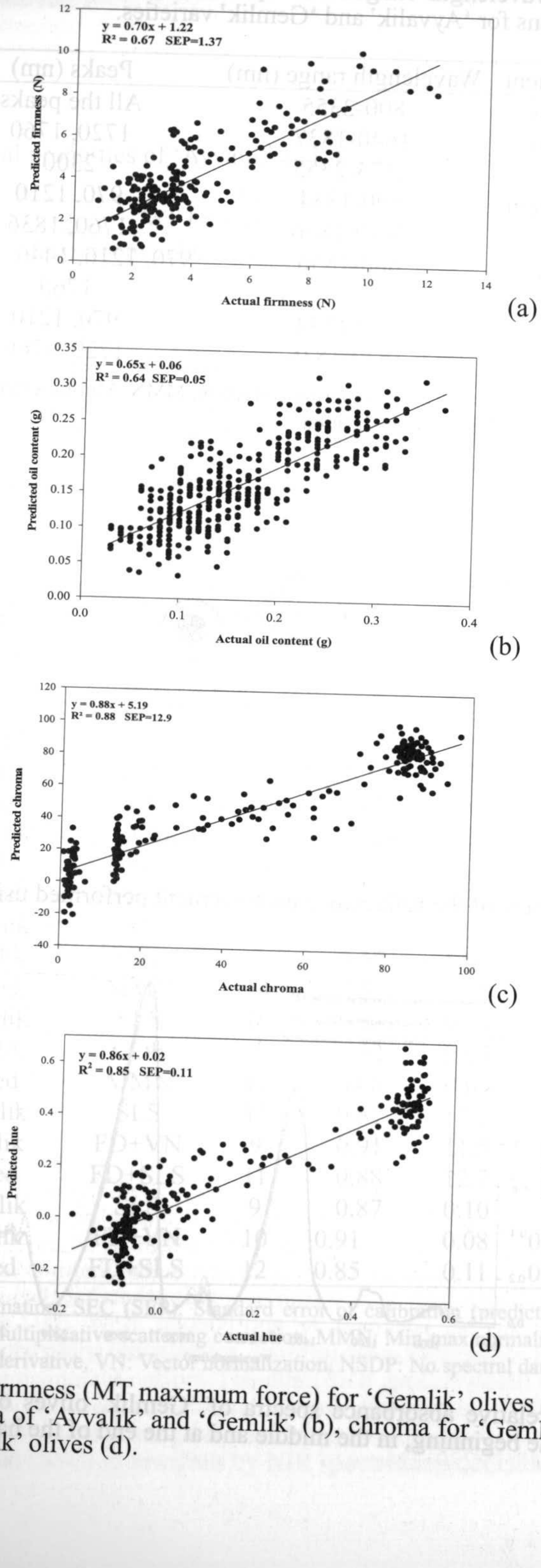

Fig. 3. Prediction of firmness (MT maximum force) for 'Gemlik' olives (a), oil content for the pooled data of 'Ayvalik' and 'Gemlik' (b), chroma for 'Gemlik' olives (c), and hue for 'Ayvalik' olives (d).